PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-081521

(43)Date of publication of application : 31.03.1998

(51)Int.Cl. C01G 53/00
H01M 4/58
H01M 10/40

(21)Application number : 08-251022

(22)Date of filing : 02.09.1996

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(54) NICKEL-MANGANESE-BASED DOUBLE HYDROXIDE, ITS PRODUCTION AND RAW MATERIAL FOR ANODE ACTIVE MATERIAL FOR LITHIUM SECONDARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a Ni-Mn-based double hydroxide having spherical shape and capable of providing a raw material for an anode active material for a lithium secondary cell having improved initial service capacity and retention of discharge by aging a precipitate obtained by performing an alkaline hydrolysis of a mixed aqueous solution of Ni and Mn salts in the presence of a specific chelating agent.

SOLUTION: This Ni-Mn-based double hydroxide is produced by adding 0.2-4.0mol chelating agent having chelating ability at Ni and Mn metal ions, and 1.1-3.0mol alkali based on 1mol Ni and Mn salts to a mixed salt aqueous solution containing 0.5-3.5mol/L Ni and Mn salts, performing an alkaline hydrolysis thereof at 10-100°C for 1-72hr while keeping the pH of the reaction liquid at 9-12 to form a precipitate, aging the precipitate obtained by precipitating nickel hydroxide and manganese hydroxide to provide the objective manganese- cobalt based double hydroxide having ≤3 particle distribution (V98-V5)/V50 measured by a laser method and (0.01:0.99) to (0.99:0.01) atomic ratio of Ni to Mn (Ni:Mn).

LEGAL STATUS

[Date of request for examination] 23.10.2002

[Date of sending the examiner's decision of rejection]

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CLAIMS

[Claim(s)]
[Claim 1] Particle size distribution which are the crystal grain children of a nickel-Mn system compound hydroxide generated in the state of a dissolution condition of nickel and Mn, and/or coprecipitation, and this crystal grain child searched for by measuring method by the laser method (V95-V5) A nickel-Mn system compound hydroxide characterized by /V50 being three or less.
[Claim 2] A nickel-Mn system compound hydroxide according to claim 1 which has an atomic ratio of nickel and Mn, and nickel:Mn in the range of 0.01:0.99 to 0.99:0.01.
[Claim 3] A manufacture method of a nickel-Mn system compound hydroxide characterized by making a precipitate generation reaction by alkali hydrolysis perform continuously under existence of a chelating agent which has complexing force to a metal ion of nickel and Mn in a mixed salt aqueous solution of nickel salt and Mn salt, making precipitate of nickel hydroxide and manganese hydroxide generate subsequently, and making this precipitate come to ripe.
[Claim 4] A successive reaction is the manufacture method of a nickel-Mn system compound hydroxide according to claim 3 performed at a multistage ceremony.
[Claim 5] A manufacture method of a nickel-Mn system compound hydroxide according to claim 3 or 4 that a chelating agent is at least one sort chosen from an amino carboxylic acid, hydroxy acid, or ammonia, or two sorts or more.
[Claim 6] A raw material for positive active material for lithium secondary batteries which makes an active principle a nickel-Mn system compound hydroxide according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to a nickel-Mn system compound hydroxide, its manufacture method, and the positive-active-material raw material for lithium secondary batteries.
[0002]
[Description of the Prior Art] The lithium secondary battery is put in practical use as a power supply of small electronic equipment as portable-izing of consumer electronics and cordless-ization progress quickly in recent years. About this lithium secondary battery, since the report ["material research brain trust" vol115, P783-789 (1980)] that it was useful as a positive-electrode active substance of a cobalt acid lithium secondary battery was made by Mizushima etc. 1980, the research and development about a lithium system multiple oxide are furthered actively, and many proposals have been made until now.
[0003] They are Li1-a NiO2 (however, 0<=a<=1) (the United States Patent number No. 4302518 specification), Lib nickel2-b O2, and LiNi1-d Cod O2. (However, 0.84<=b<=1.22, 0.09 <=b0.5) It is the multiple oxide which makes a subject a lithium and transition metals, such as LinNimCo1-m O2 (JP,63-299056,A, JP,1-120765,A, JP,1-294364,A, JP,5-290890,A, JP,6-275274,A, JP,7-142056,A), (JP,2-40861,A). In the above-mentioned compound, although it had inquired early most since a cobalt acid lithium was comparatively easy to compound, there was a problem of rarity in the cobalt (Co) of a raw material at an expensive price and in resource. Although the lithium oxide which used nickel (nickel) and Mn instead of Co is studied in order to solve this problem, it is not yet put in practical use.
[0004]
[Problem(s) to be Solved by the Invention] Manufacture on industrial level is not carried out very difficultly by composition of a nickel acid lithium. In order to solve this problem, the oxide which replaced some nickel acid lithiums nickel from Mn is proposed. However, these oxides had the problem that the dissolution reaction of nickel and Mn did not progress well, in order to compound at low temperature.
[0005] Therefore, the purpose of this invention is to offer a nickel-Mn system compound hydroxide useful as a raw material of the Li-nickel-Mn system multiple oxide used for positive electrodes, such as a lithium secondary battery, and its manufacture method.
[0006]
[Means for Solving the Problem] In this actual condition, this invention persons came to complete this invention, as a result of inquiring wholeheartedly.
[0007] That is, this invention is the particle size distribution which are the crystal grain children of a nickel-Mn system compound hydroxide generated in the state of a dissolution condition of nickel and Mn, and/or coprecipitation, and this crystal grain child searched for by measuring method by the laser method. (V95-V5) A raw material for positive active material for lithium

secondary batteries which makes an active principle a nickel-Mn system compound hydroxide and this which are characterized by /V50 value being three or less is offered.
[0008] Moreover, this invention makes a precipitate generation reaction by alkali hydrolysis perform continuously under existence of a chelating agent which has complexing force to nickel in a mixed salt aqueous solution of nickel salt and Mn salt or a metal ion of Mn, subsequently makes precipitate of cobalt hydroxide and manganese hydroxide generate, and offers a manufacture method of a nickel-Mn system compound hydroxide characterize by make this precipitate come to ripe.
[0009]
[Embodiment of the Invention] The nickel-Mn system compound hydroxide of this invention is a nickel-Mn system compound hydroxide generated in the state of dissolution with nickel and Mn, and/or coprecipitation. nickel and Mn are not only being mixed and nickel and Mn are carrying out coprecipitation mixture of what nickel and Mn generated in the state of dissolution and/or coprecipitation at homogeneity. When nickel or Mn which has not dissolved or coprecipitated exists independently, the peak of the hydroxide of nickel or Mn is checked as an impurity which originated in existence of these nickel or Mn, and was generated according to the X diffraction. However, the nickel-Mn system compound hydroxide of this invention has very few these impurities, and those peaks hardly exist in a parenchyma top powder X diffraction.
[0010] Moreover, the crystal grain children of the nickel-Mn system compound hydroxide of this invention are the particle size distribution searched for by the measuring method by the laser method. (V95-V5) /V50 value is the thing of three or less range, and it is especially desirable that it is the range of 0.5-2. Moreover, as the above-mentioned crystal grain child's mean particle diameter, 1-50 micrometers is desirable and it is especially desirable that it is the range which is 5-20 micrometers. The range of particle size becomes large and what separated from this range does not have it as a raw material for lithium secondary batteries. [so desirable] Moreover, V95, V50, and V5 95 volume %, 50 volume %, and 5 volume % are shown, respectively. the above-mentioned crystal grain child -- such -- substantial -- a spherical particle -- it is -- for example, -- true -- it is the particle of the shape of the shape of spherical or a cocoon which some ellipse-like particles and spherical particles combined, or a dumpling.
[0011] atomic ratio nickel:Mn of the nickel-Mn system compound hydroxide of this invention is 0.01:0.99 to 0.99:0.01, and is desirable -- 0.1:0.9 to 0.9:0.1 it is .
[0012] the manufacture method of the nickel-Mn system compound hydroxide of this invention performs the precipitate generation reaction by alkali hydrolysis continuously using the chelating agent which has the complexing force to the metal ion of nickel and Mn in the mixed salt aqueous solution of nickel salt and Mn salt -- making -- and a precipitate product -- necessity -- and it is fully aging, for example, the thing which makes it pile up for at least 3 hours or more, and advances an aging reaction.
[0013] Although it will not be restricted especially if nickel salt used by the manufacture method of this invention is dissolved in water, the mineral-acid salts of the water-solubility of a nickel sulfate, nickel nitrate, a nickel chloride, etc. are mentioned, for example. Moreover, although it will not be restricted especially if Mn salt as well as Co salt is dissolved in water, the mineral-acid salts of the water-solubility of a manganese sulfate, manganese nitrate, a manganese chloride, etc. are mentioned, for example. nickel salt and Mn salt, and 0.5-3.5 The aqueous solution concentration about a mol / L is preferably used for a reaction in the practical range.
[0014] Moreover, as a chelating agent which has the complexing force to these metal ions, hydroxy acid and those salts, or ammonia, such as amino carboxylic acids, such as a hydrazine, triethanolamine, a glycine, an alanine, an asparagine, iminodiacetate, glutamic acid, ethylenediamine, and ethylenediaminetetraacetic acid, and those salt; acetic acids, a lactic

acid, oxalic acid, a malonic acid, a malic acid, a tartaric acid, a citric acid, a salicylic acid, and thioglycolic acid, is mentioned, for example. Moreover, ammonia will not be especially restricted, if ammonium ion can be supplied, but although the aqueous solution of ammonium salt, such as an ammonium nitrate, an ammonium sulfate, and an ammonium chloride, aqueous ammonia, ammonia gas, etc. are mentioned, for example, it is aqueous ammonia preferably.

[0015] The amino carboxylic acid, the above-mentioned hydroxy acid, and above-mentioned ammonia of a chelating agent may be used combining one sort or two sorts or more, and receive nickel salt and one mol of Mn salts as the loadings. 0.2-4.0 The range of a mol is desirable. In addition, especially as the combination method of a chelating agent, it may not be restricted, but it may be used independently, or any of nickel salt water solution and Mn salt water solution or a predetermined rate may be mixed beforehand, and you may add. less than 0.2 mols -- particle growth -- not enough -- moreover -- In 0.4 mols or more, it is not desirable from an economical field.

[0016] Moreover, as alkali used for alkali hydrolysis, caustic alkali aqueous solutions, such as a sodium hydroxide and a potassium hydroxide, are mentioned, among these a sodium hydroxide is desirable. The addition of alkali receives nickel salt and one mol of Mn salts. 1.1-3.0 It is a mol. in the case of less than 1.1 mols, unreacted nickel salt and Mn salt generate and are not desirable -- the non-grown up particle whose grain child growth exceeding 3.0 is not enough generates mostly and is not desirable.

[0017] The method of making pile up for at least 3 hours, and making it react is mentioned making pH of the reaction mixture added continuously, for example hold to the constant value of the range of 9-12 especially as this reaction actuation, although not restricted. At this time, reaction mixture may carry out an aging reaction with the following container made to overflow once.

[0018] Moreover, it is the method of making it react, controlling the capacity of reaction mixture to a constant rate only except for reaction data-medium liquid, without making the liquid of the system of reaction which adds reaction mixture continuously and includes a resultant as other methods overflow. Since it grows up continuously, it increases and stirring of the system of reaction becomes difficult gradually, before being in such a condition, as for the particle of the nickel-Mn compound hydroxide formed in a reaction container, it is desirable according to this method, to terminate a reaction.

[0019] As for the slurry concentration of this system of reaction, it is desirable to set up a reaction condition so that it may become at least 70 or more g/L. Since the grain child growth with thin concentration becomes extremely slow rather than this, it is not desirable.

[0020] although you may add continuously at once, the multistage method which boils several times, divides and is dropped in multistage is sufficient as each reaction mixture to add.

[0021] 10-100 degrees C of reaction temperature are usually 20-80 degrees C preferably, and reaction time is about 1 - 72 hours.

[0022]

[Effect of the Invention] The nickel-Mn system compound hydroxide of this invention has the spherical shape of particle substantially, and is useful as a raw material for positive active material for lithium secondary batteries, and the lithium secondary battery which used positive active material by making the nickel-Mn system multiple oxide concerned into an active principle has the outstanding property which is not in the former, such as initial discharge capacity and discharge retention.

[0023]

[Example] Next, although an example is given and this invention is explained concretely, this is only instantiation and does not restrict this invention.

[0024] They are a flare and this about 200ml water beforehand to an example 11L beaker.

NiSO4 and 7H2 O of 1.6 mol/L 400ml of ammonia liquor of 14.8 mol/L was added by the dropping method as 1200ml of mixed liquor of MnSO4 and 5H2 O of 0.4 mol/L, 800ml of NaOH solutions of 6 mol/L, and a complexing agent, adjusting pH to 11, it was kept warm at 50 degrees C, and stirring aging was carried out for 9 hours. The volume in a system was controlled by the overflow method in the meantime, and the reaction mixture of a constant rate was discharged. Next, repulping washing of the crystal after filtration was carried out, and the cleaning effect was checked with the electric conductivity meter. the eutectic object which generated this crystal in the state of dissolution of nickel and Mn, and/or coprecipitation -- it is -- a presentation -- mole ratio of nickel:Mn 0.8:0.2 it was . When the particle size distribution of this crystal were measured by the laser method, it is /(V95-V5) V50 value. Mean particle diameter was 9 micrometers in 1.0.

[0025] They are a flare and this about 200ml water beforehand to an example 21L beaker. NiSO4 and 7H2 O of 0.4 mol/L 400ml of glycine solutions of 1 mol/L was added by the dropping method as 1200ml of mixed liquor of MnSO4 and 5H2 O of 1.6 mol/L, 800ml of NaOH solutions of 6 mol/L, and a complexing agent, adjusting pH to 10, it was kept warm at 70 degrees C, and stirring aging was carried out for 9 hours. The volume in a system was controlled by the overflow method in the meantime, and the reaction mixture of a constant rate was discharged. Next, repulping washing of the crystal after filtration was carried out, and the cleaning effect was checked with the electric conductivity meter. the eutectic object which generated this crystal in the state of dissolution of nickel and Mn, and/or coprecipitation -- it is -- a presentation -- mole ratio of nickel:Mn 0.2:0.8 it was . When the particle size distribution of this crystal were measured by the laser method, it is /(V95-V5) V50 value. Mean particle diameter was 10 micrometers in 1.1.

[0026] They are a flare and this about 250ml water beforehand to 3500ml beaker of examples. NiSO4.7H2 O of 0.2 mol/L 670ml of malic-acid solutions of 1 mol/L was added by the dropping method as 1300ml of NaOH solutions and the complexing agent of mixed liquor 2L of MnSO4 and 5H2 O of 1.8 mol/L, and 6 mol/L, adjusting pH to 10, it was kept warm at 70 degrees C, and stirring aging was carried out for 15 hours. In order to control the volume in a system in the meantime, slurry concentration was raised removing only reaction data-medium liquid by the reduced pressure **** method. Next, repulping washing of the crystal after filtration was carried out, and the cleaning effect was checked with the electric conductivity meter. the eutectic object of nickel and Mn which generated the crystal after desiccation in the state of dissolution and/or coprecipitation -- it is -- a presentation -- mole ratio of nickel:Mn 0.1:0.9 it was . When the particle size distribution of this crystal were measured by the laser method, the mean particle diameter of /(V95-V5) V50 value was 9 micrometers in 1.7.

[Translation done.]